Concentration-Dependent Time-Lag Measurements

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In gas-metal permeation, diffusion is normally considered to be the rate-controlling step. In addition, the diffusivity is usually taken to be independent of concentration. Under these conditions, the time lag (a characteristic of the system which depends on the time required to achieve steady state flow) is found to be (and theoretically should be) independent of the gas pressure applied to the inlet surface of the metal membrane. Furthermore, the time lag can then be directly related to the diffusivity of the system.

In this paper, data on the hydrogen type 321 stainless steel system are presented which show a pronounced effect of pressure on measured values of the time lag. Taken alone, these data can be explained either by a concentration-dependent diffusivity or by resistance to flow at the metal surface. From steady state data it is shown that surface resistance is the better explanation. A model of the permeation process is presented which is consistent with the time lag data, and an estimate is made of the diffusivity of hydrogen in type 321 stainless steel.

The variables studied were hydrogen pressure at the entrance surface of the membrane (0.1 to 30.0 atm.), temperature (300° to 800°C.), and membrane wall thickness (0.0252 to 0.2475 cm.).

Determining the diffusivity of a gas in a metal is difficult because of the problems associated with measuring gas concentration within the metal. A method called the *time-lag method,* which depends only upon the time required to achieve steady state flow in a permeation experiment, is therefore frequently used (*4*). For a system in which diffusion is the rate-controlling step and the diffusivity is independent of concentration, time-lag measurements are found to be (and theoretically should be) independent of the gas pressure applied to the inlet surface of the metal membrane. When departures from this behavior have been observed, the magnitude of the departure has been small and usually explained by a concentration-dependent diffusivity.

The purpose of this paper is to present data which show a strong dependence of measured values of time lag on the inlet gas pressure. It is shown that these data behave in a reasonable manner. Furthermore, a model, based on resistance to flow at the metal surface, is presented which explains the observed data.

The data presented here were obtained in connection with measurements made on the hydrogen type 321 stainless steel system which were reported in an earlier paper (*25*). The time-lag data were not reported at that time as they were not considered pertinent.

TIME-LAG THEORY

The time-lag method was first applied by Daynes (*14*) to the diffusion of gas through rubber membranes and later extended by Barrer (*5* to *7*) to gas-metal diffusion. The theory and mathematical treatment of the time lag are discussed in several references (*4, 11*). It is appropriate to present here only those results that will be of value in analyzing our data.

Illustration of the Time Lag

Consider an initially gas-free membrane which is suddenly subjected to a constant hydrogen pressure on one side, while pressure on the other side is maintained essentially equal to zero. If one plots the total quantity of gas which has permeated through the membrane as a function of time of exposure to hydrogen, the result will be as shown in Figure 1. The curve initially goes through an unsteady state period (required for the concentration gradient to form in the membrane) and then tends asymptotically to the steady state. The intercept on the time axis, obtained by extrapolating back from the steady state region, is called the *time lag.* (Figure 1 is typical of the experimental results obtained in this work.)

Relation of the Time Lag to Diffusivity

Barrer (*6*) has shown that when the concentrations are c_1 on the ingoing side, c_2 on the outgoing side, and c_o initially in the membrane, and the diffusivity D is independent of concentration, the time lag L for diffusion through a slab of thickness is given by

$$L = \frac{1}{(c_1 - c_2)} \left[\frac{c_1 l^2}{6D} + \frac{c_2 l^2}{3D} - \frac{c_o l^2}{2D} \right] \tag{1}$$

For the usual experimental case, $c_o = 0$ and $c_2 = 0$ (that is, exit pressure is essentially zero). Under these conditions, Equation (1) reduces to

$$L = \frac{l^2}{6D} \tag{2}$$

Jaeger (*20*) has shown that for a cylinder the equation analogous to Equation (2) is

$$L = \frac{r_1^2 - r_2^2 + (r_1^2 + r_2^2) \ln r_2/r_1}{4D \ln r_2/r_1} \tag{3}$$

A surprising consequence of Equations (2) and (3) is that the time lag is independent of the actual concentration maintained at the entrance surface. However, as dictated by the boundary conditions, Equations (2) and (3) are valid only for a system in which c_1 remains constant and D is independent of concentration. Furthermore, these simple relations will hold only if surface reactions are not rate controlling.

For purposes of analysis, the cylindrical permeation membranes used in this work were treated as slabs. Little error is introduced by calculating D from Equation (2) instead of (3).

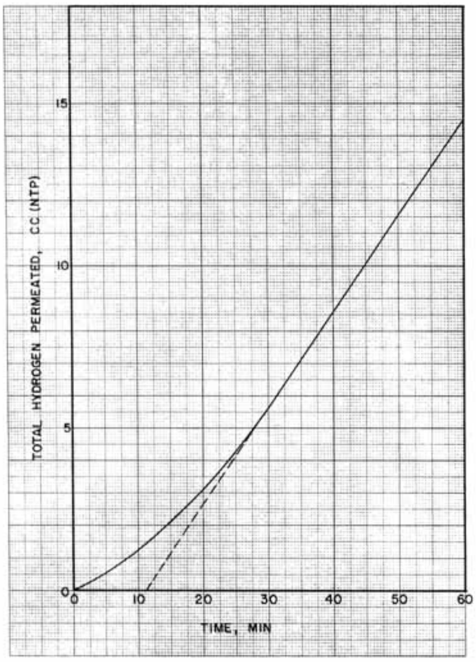

Fig. 1. Illustration of time lag.

The Effect of Surface Resistance on the Time Lag

In gas-metal permeation work, that gas concentration just inside the metal surface is normally assumed to be in equilibrium with the applied gas pressure. In the case of hydrogen, the solubility relation (at constant temperature) is expressed by (*27*)

$$c = Kp^{1/2} \tag{4}$$

The actual processes which take place at the metal surface during permeation are quite complicated. Fast (*15*) has analyzed the process of gas permeation through metals into five steps and has presented evidence that under the proper conditions each of these steps may be rate controlling. Attempts (*3, 12*) have been made to include all possible rate expressions in a steady state permeation expression. However, even for the steady state case, the resulting expressions are so complicated as to be essentially useless. Very few attempts have been made to include realistic boundary conditions in analyzing unsteady state permeation. If there is resistance to flow at the metal surface, Equation (4) does not hold. Under these conditions, Barrer (*4*) points out that L becomes a complicated function of the appropriate rate constants at the surface and D.

In an earlier paper, Phillips and Dodge (*25*) presented a model for taking into account slow surface reactions in the permeation process which included one arbitrary constant a transfer coefficient at the inlet surface of the metal membrane. For steady state and a cylindrical permeation membrane, the final form of the equation presented was

$$R = \frac{A_a p_1^{1/2}}{\dfrac{(r_2 - r_1)}{KD} + \dfrac{1}{h}} \tag{5}$$

where h is defined by

$$R = A_a h\,(p_1^{1/2} - c_1/K) \tag{6}$$

As can be seen when h is large, Equation (5) reduces to

$$R = A_a DKp_1^{1/2}/(r_2 - r_1) \tag{7}$$

Equation (7) is the Richardson equation (*26*) and is normally used in analyzing gas-metal permeation work. The Richardson equation assumes equilibrium between gas dissolved in the metal and the applied gas pressure and says that the permeation rate is inversely proportional to membrane thickness and proportional to the square root of pressure.

For the case where $1/h$ is large compared with $(r_2 - r_1)/KD$, Equation (5) reduces to

$$R = A_a h p_1^{1/2} \tag{8}$$

If, as suggested by Chang and Bennett (*12*), under these conditions R is proportional to p_1, then h must be proportional to $p_1^{1/2}$.

Several studies (*21, 22, 5*) have been made, primarily with regard to the conduction of heat, which were designed to derive expressions for the time lag showing the effect of resistances in series. Of particular interest here is the work of Jaeger (*21*) who derived an expression for the time lag for heat conduction through a composite slab in terms of the thermal properties of the various wall sections.

From the work of Jaeger and the model for permeation represented by Equations (5) and (6), the following time-lag expression can be derived for permeation through a slab of thickness l:

$$L = \frac{l^2}{6D}\,\frac{\left(\dfrac{l}{KD} + \dfrac{3}{h}\right)}{\left(\dfrac{l}{KD} + \dfrac{1}{h}\right)} \tag{9}$$

If the diffusion resistance to flow l/KD is large compared with the surface resistance $1/h$, Equation (9) reduces to Equation (2). If the surface resistance is large compared with the diffusion resistance, Equation (9) reduces to

$$L = \frac{l^2}{2D} \tag{10}$$

Equations (2) and (10) say that if one is not aware that surface processes are affecting his measurements, the value of D he calculates from a given time-lag measurement could be as much as three times too small. However, this implies that any time-lag measurement will enable one to calculate D within a factor of 3. Thus, Barrer's (*7*) comment that the time lag is relatively insensitive to surface processes seems justified.

Effect of Concentration-Dependent Diffusivity on the Time Lag

The mathematics of concentration-dependent diffusion is complicated, and solutions of the diffusion equation are available for only a limited number of functional relations between D and c (*13*). In general, numerical methods must be used. However, some work has been done regarding the effect of a concentration-dependent diffusivity on the time lag (*1, 17*).

For example, in both of these papers the case has been considered where the concentration dependence of D is given by

$$D(c) = D_o(1 + mc) \tag{11}$$

The resulting time-lag equation is (for small m and equilibrium at the gas entry surface)

$$L = \frac{l^2}{6D_o}\,\frac{(1 + \frac{1}{4} mKp_1^{1/2})}{(1 + \frac{1}{2} mKp_1^{1/2})} \tag{12}$$

Equation (12) indicates that L decreases with increasing pressure, and that at very high pressures the time lag is given by the limiting expression $L = l^2/12D_o$ which is similar to Equation (2).

It is of interest, at this point, to examine the effect of concentration-dependent diffusivity on the steady state permeation relation. Bryan (*9*) and Benkiki (*8*) studied the diffusion of hydrogen in pure iron and interpreted their results in terms of a concentration-dependent diffusivity of the form

$$D = D_o(1 - e^{-mc}) \qquad (13)$$

From this relation, the following equation was derived which is analogous to Equation (7):

$$R = \frac{AD_o}{l}\left[Kp_1^{1/2} - \frac{1}{m}\left(1 - e^{-Kmp_1^{1/2}} \right) \right] \qquad (14)$$

An important point is illustrated by Equation (14). If concentration-dependent diffusivity is the cause of an observed deviation from the Richardson equation (actually deviation from the square-root-of-pressure relationship), the rate is still inversely proportional to the membrane thickness. However, Equation (5) states that the inverse thickness relation will not hold if surface reactions are causing the deviation.

EXPERIMENTAL

Detailed descriptions of the experimental system, procedure, and equipment used to obtain the data discussed here have been presented previously (*25, 24, 10*). Only those features of particular interest will be reviewed.

Experimental System and Range of Variables

The gas-metal system used in this work was hydrogen AISI type 321 stainless steel. Type 321 stainless steel is a titanium stabilized, austenitic (18-8) stainless, whose general properties are well known (*23*). This system was selected because Flint (*16*) had speculated that surface processes might slow the hydrogen permeation rates.

The permeation membranes themselves were fabricated from commercial aircraft quality, seamless, cold drawn tubing. The important dimensions of the four membranes used are presented in Table 1. A more complete description of the membranes is available (*24*).

Four permeation cells were fabricated as shown in Figure 2. The permeation cells were made entirely of type 321 stainless steel, and each cell was identical except for the difference in membrane wall thickness. Appropriate tubing provided cold connections to the high pressure (gas delivery) and vacuum (gas collecting) systems.

The inside (gas entry) surface of each membrane was mechanically polished to a mirror finish in an attempt to slow the surface reactions as much as possible (*19*) and to localize any observed interfacial resistance at the entry surface.

The variables studied were hydrogen pressure at the entrance surface of the permeation membrane (0.1 to 30.0 atm.), temperature of the permeation membrane (300° to 800°C.), and membrane wall thickness (0.0252 to 0.2475 cm.).

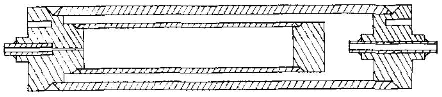

Fig. 2. Permeation cell.

TABLE 1. DIMENSIONS OF PERMEATION MEMBRANES

Membrane	I.D., (cm.)	$(r_2 - r_1)$, (cm.)	A_a, (sq. cm.)
A	2.0386	0.2475	164.2
B	2.3482	0.1011	175.9
C	2.3476	0.1003	175.8
D	2.4977	0.0252	181.2

Experimental Procedure and Equipment

The basic experimental technique used in this work to measure permeation rates and the associated time lags has been used many times in the past (*7, 9, 18*). Briefly, it was as follows. After the desired temperature level was achieved, hydrogen was charged to the inside surface of a previously degassed metal membrane. A constant hydrogen pressure was then maintained on the membrane, while the exit surface was maintained under a high vacuum by pumping the permeated gas away.

As discussed with regard to Figure 1 the permeation rate initially goes through an unsteady state period as the hydrogen concentration gradient develops within the metal, until the steady state is achieved. The rate of permeation was determined by measuring the rate of pressure rise in a gas-collecting system of known volume. (A mercury diffusion pump was used to pump gas away from the exit surface of the membrane and into the collecting system where pressure was measured with a modified McLeod gauge.) The temperature of the gas in the collecting system was measured and the rate of permeation calculated from the ideal gas law.

To obtain meaningful time-lag data it is important that the permeation membrane be sufficiently degassed between runs. To insure this, a blank run (with vacuum maintained on the gas delivery side of the membrane) was made prior to each run. In general the membranes were degassed anywhere from 5 to 40 hr. between runs, depending on the temperature and membrane thickness.

EXPERIMENTAL RESULTS

Calculation Procedure

Graphical determination of the time lag often requires a long, and possibly inaccurate, extrapolation. Therefore, a Fortransit program was written for calculating the basic quantities of interest, the permeation rate, and the time lag from the raw experimental data of a given run. If the experimental technique used in this work is followed, the program developed is quite general in its application to the required permeation calculations. The Fortransit listing and a flow diagram of the program are available (*24*).

The basic data were recorded and read into the machine in the form of pressure-time measurements, along with the collecting volume and temperature. The blank rates observed before each run were calculated as part of the program by a least-squares straight line through the blank pressure vs. time data. The program was written so that the blank pressure vs. time curve so calculated could be extrapolated and subtracted point-by-point from the permeation pressure vs. time data, thus eliminating the effect of blank rates on the final results.

At least five good pressure vs. time points were required in the steady state permeation region. The machine then calculated the standard deviation of the four resulting pressure-time increments and included in the final calculation (in sequence) those additional data points that did not increase the standard deviation (thus preventing the inclusion of points from the unsteady state region).

Finally, the machine computed a least-squares straight line through the points that it found acceptable. From this line, the permeation rate *R* and the time lag *L* were determined.

Typical Time-Lag Results

Time-lag data which are typical of those obtained in this work are presented in Table 2. Data are presented for the three instances in which it was possible to obtain time-lag measurements at three different pressures at about the same temperature on a given membrane. Additional data obtained at two pressures at 300°C. are included to extend the temperature range of the data to be discussed.

Table 2. Typical Time-Lag Data

Membrane	Temperature, (°C.)	Pressure, (atm.)	Time lag. (min.)
B	605.	.120	20.7
($l = 0.1011$ cm.)	603.	1.03	11.2
	597.	1.02	11.2
	602.	10.9	6.5
B	396.	1.01	83.1
($l = 0.1011$ cm.)	395.	10.1	52.1
	392.	10.2	60.4
	395.	29.1	52.8
A	398.	1.04	542.
($l = 0.2475$ cm.)	398.	10.1	383.
	398.	30.4	313.
C	302.	1.04	327.
($l = 0.1003$ cm.)	301.	30.1	238.

All of the data obtained in this work showed the same general behavior of time lag with pressure as is indicated in Table 2. However, subsequent discussion and analysis will be restricted to those data presented in Table 2.

There are two interesting features of the results presented in Table 2. One is simply the wide range of time-lag values measured, from 6½ to 542 min. (about 9 hr.).

The second and most important feature is the pronounced effect of pressure on the time lag. The effect reported here is more pronounced than in any known similar results for a gas-metal system. In one case more than a threefold variation was noted over the pressure range indicated. From logarithmic plots of the data, exponents of from 0.1 to 0.7 were found to describe the effect of pressure on the time-lag data presented in Table 2.

ANALYSIS OF RESULTS

Prediction of Diffusivity from Time-Lag Measurements

If one postulates that for a given system the time lag will become independent of pressure at a sufficiently high pressure, then above that pressure Equations (2) and (3) will hold. Note that this follows directly from Equations (12) and (9) if one assumes that h increases with increasing pressure. Furthermore, virtually all steady state hydrogen permeation data obey the square-root-of-pressure law for some pressure range. One should expect the time lag to be independent of pressure over the same pressure range.

This postulated behavior was used to establish reasonable values of the diffusivity for the hydrogen type 321 stainless steel system. The time-lag data presented in Table 2 were plotted vs. $1/p^{1/2}$ (at constant temperature), and an extrapolation was made to $1/p^{1/2} = 0$. Values of D were then calculated from Equation (3) by using the extrapolated time-lag values. The results are plotted in Figure 3. (It might be noted that the extrapolations were in any case not great.)

As shown in Figure 3, a plot of log D vs. $1/T$ is represented surprisingly well by a straight line from which an activation energy of diffusion of 12,500 cal./g. mole was calculated. The data in Figure 3 are represented by the equation

$$D = D_0 \exp\left(-\frac{E_d}{RT}\right) = 0.44 \exp\left(-\frac{12{,}500}{RT}\right) \tag{15}$$

For comparison, an estimate was made of the value of hydrogen diffusivity in type 347 stainless steel with the permeation data of Flint (*16*) and the solubility data of Armbruster (*2*). (Flint found that this system exhibited normal permeation behavior as represented by the Richardson equation.) The values calculated were $D = 1.74 \times 10^{-4}$ sq.cm./min. at 600°C. and $D = 1.81 \times 10^{-5}$ sq.cm./min. at 400°C. For the hydrogen type 321 stainless steel system the corresponding values are [Figure 3 or Equation (15)] $D = 3.3 \times 10^{-4}$ sq.cm./min. at 600°C. and $D = 3.5 \times 10^{-5}$ sq.cm./min. at 400°C. Thus the values of D shown in Figure 3 are of a reasonable order of magnitude. The fact that hydrogen diffusivity is

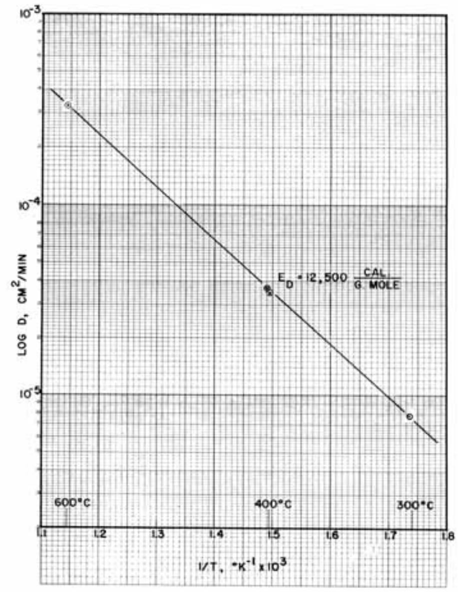

Fig. 3. Log of diffusivity vs. reciprocal of absolute temperature.

Table 3. Constants for Interfacial-Resistance Model Time-Lag Data

Conditions	Pressure, (atm.)	D^*, (sq. cm./min.)	h, $\left[\frac{\text{cc. (NTP)}}{\text{min. (atm.)}^{1/2}\text{ sq. cm.}}\right]$	$\frac{KD}{hl}$
Membrane *B*	0.120	—	—	—
~603°C.	1.03	3.3×10^{-4}	1.3×10^{-3}	1.4
	10.9	3.3×10^{-4}	$12. \times 10^{-3}$	0.15
Membrane *B*	1.01	3.6×10^{-5}	2.0×10^{-4}	0.61
~395°C.	10.2	3.6×10^{-5}	7.5×10^{-4}	0.16
	29.1	3.6×10^{-5}	$20. \times 10^{-4}$	0.06
Membrane *A*	1.04	3.6×10^{-5}	0.59×10^{-4}	0.84
~398°C.	10.1	3.6×10^{-5}	2.4×10^{-4}	0.21
	30.4	3.6×10^{-5}	9.1×10^{-4}	0.05
Membrane *C*	1.04	7.9×10^{-6}	0.5×10^{-4}	0.37
~302°C.	30.1	7.9×10^{-6}	2.8×10^{-4}	0.06

* Values obtained from time lag at $1/p^{1/2} = 0$

higher in 321 stainless steel than in 347 is not surprising since 321 contains titanium, and hydrogen is very soluble in titanium. Thus, relatively high values of D might be expected (*19*).

An estimate was also made of the solubility of hydrogen in type 321 stainless steel. If one takes the permeation rate, measured at the highest pressure at a given temperature, and the corresponding value of D presented in Figure 3, the solubility K may be calculated by assuming that Equation (7) is valid. An Arrhenius plot of the calculated values of K also shows an unexpectedly good correlation, which can be represented by

$$K = K_o \exp(-E_s/RT) = 32.2 \exp(-3{,}000/RT) \tag{16}$$

From Equation (16), the following values of K, cc.(NTP)/cc.(atm.)$^{1/2}$, may be calculated: $K = 0.571$ at 600°C. and $K = 0.336$ at 400°C. For comparison, the corresponding values given by Armbruster (*2*) are $K = 0.372$ at 600°C. and $K = 0.26$ at 400°C. Again the higher solubilities in type 321 stainless steel might be expected owing to the presence of titanium.

Analysis of Time-Lag Data with the Interfacial Resistance Model

Taken by themselves, the data in Table 2 can be explained equally well by either a slow surface step or a concentration-dependent diffusivity. To distinguish between these possibilities, consideration must be given to the steady state data. Using membrane thickness as a variable, Phillips and Dodge (*25*) have established that slow surface steps are very important in the hydrogen type 321 stainless steel system. They used Equation (5) to correlate their rate data at four different membrane thicknesses.

From the steady state data it appears that slow surface reactions were causing departure from the Richardson equation. If true, the type of variation of the time lag with pressure reported here was to be expected, and the interfacial resistance model [Equation (9)] represents a plausible means of explaining the transient data.

Table 3 presents the results of applying Equation (9) to the time-lag data, from the values of D previously calculated. As can be seen, the relative value of interfacial resistance to diffusion resistance, represented by the term KD/hl, decreases with increasing pressure. Values of h, the surface transfer coefficient, are found to increase with increasing pressure and temperature. The transfer coefficient h is seen to vary approximately with the square root of pressure except for the abnormally strong pressure dependence shown at 600°C.

Two anomalies show up in Tables 2 and 3. First, at 600°C. the time lag was found to vary by more than threefold over the experimental pressure range. Equation (10) predicts a maximum variation of threefold.

A second anomaly is that at a given temperature and pressure h was not constant from membrane to membrane. (For the data shown a comparison can be made at approximately 400°C.) This result is not surprising when one considers the number of factors which may influence the surface reactions (*19*), but it does point up the fact that the model must be considered a method for explaining the data and not a prediction method.

In summary, two phenomena, namely concentration-dependent diffusivity and slow surface reactions, may cause departures from normal permeation behavior. (It is, of course, possible that both may be present simultaneously.) For a given gas-metal system, if one observes unusual steady state behavior, he should expect unusual transient behavior at the same conditions of temperature and pressure. Furthermore, the permeation mechanism should be the same for the transient and steady state cases. Thus it can be seen that the hypothesis of a slow surface reaction explains the observed time-lag data better because it clearly explains the steady state data better.

Comparison of Time-Lag and Steady State Results

From the transient data it was found that h increased with increasing pressure and temperature. The same general trend in h can be demonstrated by using steady state results. Table 4 presents steady state information obtained from two different methods. First, the principal results of

TABLE 4. CONSTANTS FOR INTERFACIAL-RESISTANCE MODEL STEADY STATE DATA

Variable thickness*

Temperature, (°C.)	Pressure, (atm.)	D, sq. cm./min.	$h \left[\frac{\text{cc. (NTP)}}{\text{min. (atm.)}^{1/2}\text{ sq. cm.}}\right]$
608	1.0	4.1×10^{-4}	4.7×10^{-3}
604	0.1	4.0×10^{-4}	2.3×10^{-3}
401	1.0	5.1×10^{-5}	1.4×10^{-4}

Variable pressure

Conditions	Pressure, (atm.)	D, sq. cm./min.	$h, \left[\frac{\text{cc. (NTP)}}{\text{min. (atm.)}^{1/2}\text{ sq. cm.}}\right]$	$\frac{KD}{hl}$
Membrane *B*	0.120	3.3×10^{-4}	4.6×10^{-3}	0.40
603°C.	1.03	3.3×10^{-4}	$16. \times 10^{-3}$	0.12
	10.9	3.3×10^{-4}	1.1	0.002
Membrane *B*	1.01	3.6×10^{-5}	5.7×10^{-4}	0.22
395°C.	10.2	3.6×10^{-5}	$78. \times 10^{-4}$	0.02
	29.1	3.6×10^{-5}	Neg.	—
Membrane *A*	1.04	3.6×10^{-5}	3.0×10^{-4}	0.17
398°C.	10.1	3.6×10^{-5}	6.3×10^{-4}	0.08
	30.4	3.6×10^{-5}	Neg.	—
Membrane *C*	1.04	7.9×10^{-5}	1.6×10^{-3}	0.01
302°C.	30.1	7.9×10^{-5}	7.0×10^{-3}	0.003

* All four membranes were used for these measurements. The value of h reported at a given temperature and pressure was taken to be constant from membrane to membrane.

Phillips and Dodge (25) are presented. Here D and h were calculated from membrane thickness as the independent variable while temperature and pressure remained constant. Data were obtained on all four membranes from which one value of h was calculated which is characteristic of a given temperature and pressure. The second part of Table 4 shows values of h calculated when pressure is taken to be the independent variable. Here, for a given membrane at a given temperature, h may be calculated as a function of pressure. In both cases, Equation (5) was used as the basis for calculation.

First consider the original results of Phillips and Dodge (25) based on variable thickness. From Tables 3 and 4 it can be seen that values of D obtained from steady state and time-lag data are comparable. There is also agreement as to the general effect of temperature and pressure on h but no agreement between actual values of h evaluated at the same conditions of temperature and pressure. (Note that in the earlier work it was necessary to assume that h remained constant from membrane to membrane, at a given temperature and pressure. This assumption is apparently not valid.) The values of D presented in Table 3 were calculated from Equation (16) to determine the solubility constant K.

The use of pressure as the independent variable was applied to the steady state data obtained from the runs indicated in Table 2. The intended purpose was to show better agreement between the time-lag and steady state results by using data from the same run (and thus eliminating variation between membranes as a factor). These results are also presented in Table 4, with values of D and K obtained from the time-lag data [Equations (15) and (16)]. As can be seen, the values of h calculated this way differ more from the time-lag results than those calculated from the thickness effect. However, the general behavior of the calculated parameters is as expected. In general, the effect of pressure on the steady state permeation rates was more difficult to establish than on the time-lag values.

CONCLUSIONS

1. Time-lag data have been presented which are unusual in that measured values of the time lag are strongly dependent on the applied pressure (Table 2).

2. A model of the permeation process, based on resistance to flow at the metal surface, introduced earlier (25) has been shown to describe the time-lag data presented here as well as steady state data. Furthermore, the importance of membrane thickness as a variable is again demonstrated when an attempt is made to distinguish between the effect of resistance to flow at the membrane surface and a concentration-dependent diffusivity.

3. It has been shown that surface reactions will affect the permeation process less at higher temperatures and higher pressures.

4. The diffusivity of hydrogen in type 321 stainless steel may be estimated from

$$D = 0.44 \exp\left(-\frac{12{,}500}{RT}\right) \qquad (15)$$

NOTATION

A = area, permeation area, area perpendicular to the direction of gas flow, sq. cm.
A_a = arithmetic average permeation area for a hollow cylinder, sq. cm.
c = concentration (atomic) of gas within the metal lattice, cc. (NTP)/cc.
D = diffusivity or diffusion coefficient, sq. cm./min.
D_o = value of D at infinite temperature; value of D at some specified value of concentration, sq. cm./min.
E_d = activation energy for diffusion, cal./g.mole
E_s = activation energy for solubility or heat of solution, cal./g.mole
h = mass transfer coefficient for interfacial-resistance model, cc. (NTP)/sq. cm. min. $(\text{atm.})^{1/2}$
K = solubility constant, cc. (NTP)/cc. $(\text{atm.})^{1/2}$
K_o = solubility constant at infinite temperature, cc. (NTP)/cc. $(\text{atm.})^{1/2}$
L = time lag, min.
l = thickness of permeation membrane, cm.
m = arbitrary constant for concentration-dependent diffusivity, cc./cc. (NTP)
p = gas pressure, atm.
R = rate of permeation, total rate of gas permeation or diffusion through a metal barrier, cc. (NTP)/min.
R = molar gas constant, 1.987 cal./g.mole (°K.)
r = radial distance in a cylinder, cm.
T = absolute temperature, °K.
t = time, min.

Subscripts

1, 2 = conditions at entrance and exit surfaces, respectively, for p, c, and r
o = conditions at time equal to zero

LITERATURE CITED

1. Aitken, A., and R. M. Barrer, *Trans. Faraday Soc.*, **51**, 116 (1955).
2. Armbruster, M. H., *J. Am. Chem. Soc.*, **65**, 1043 (1943).
3. Ash, R., and R. M. Barrer, *Phil. Mag.*, **47**, 1197 (1959).
4. Barrer, R. M., "Diffusion In and Through Solids", p. 217, Cambridge Univ. Press, Cambridge, England (1941).
5. ———, *Phil. Mag.*, **28**, 148 (1939).
6. ———, *Trans. Faraday Soc.*, **35**, 628 (1939).
7. *Ibid.*, **36**, 1235 (1940).
8. Benkiki, D. L., M.E. thesis, Yale Univ., New Haven, Conn. (1956).
9. Bryan, W. L., Ph.D. dissertation, Yale Univ., New Haven, Conn. (1959).
10. ———, and B. F. Dodge, *AIChE J.*, **9**, 223 (1963).
11. Carslaw, H. S., and J. C. Jaeger, "Conduction of Heat in Solids," Oxford Univ. Press, England (1947).
12. Chang, P. L., and W. D. G. Bennett, *J. Iron Steel Inst.*, **170**, 208 (1952).
13. Crank, J., "The Mathematics of Diffusion," Clarendon Press, Oxford, England (1956).
14. Daynes, H., *Proc. Roy. Soc.*, **97A**, 286 (1920).
15. Fast, J. D., *Philips Tech. Rev.*, **6**, 365 (1941); **7**, 73 (1942).
16. Flint, P. S., Knoll's Atomic Power Laboratory, Schenectady, New York, *KAPL-659* (Dec. 14, 1951).
17. Frisch, H. L., *J. Phys. Chem.*, **61**, 93 (1957); **62**, 401 (1958); **63**, 1249 (1959).
18. Harden, K. L., M.E. thesis, Yale Univ., New Haven, Conn. (1957).
19. Holloman, J. H., ed., "Atom Movements," pp. 174-191, Am. Soc. Metals, Cleveland, Ohio (1951).
20. Jaeger, J. C., *Trans. Faraday Soc.*, **42**, 615 (1946).
21. ———, *Appl. Math.*, **8**, 187-98 (1950).
22. Levy, S., *Trans. Am. Soc. Mech. Engrs.*, *78, 1627-35* (1956).
23. "Metals Handbook," Am. Soc. Metals, Cleveland, Ohio (1948).
24. Phillips, J. R., Ph.D. dissertation, Yale Univ., New Haven, Conn. (1960).
25. ———, and B. F. Dodge, *AIChE J.*, **9**, 93 (1963).
26. Richardson, O., *Phil. Mag.*, **7**, 266 (1904); **8**, 1 (1904).
27. Sims, C. E., "Gases in Metals," pp. 119-198, Am. Soc. Metals, Cleveland, Ohio (1953).

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